USE OF LITHIUM BORATE IN NON-AQUEOUS RECHARGEABLE LITHIUM BATTERIES

[0001] This application is a continuation-in-part of application Serial No. 09/795,235, filed February 28, 2001.

FIELD OF THE INVENTION

[0002] The loss in delivered capacity upon cycling non-aqueous rechargeable lithium batteries can be reduced by treating the surface of the cathode powder with $LiCoO_2$-type structure with a small amount of lithium borate. This invention pertains to non-aqueous rechargeable lithium batteries and to methods for improving the performance thereof.

BACKGROUND OF THE INVENTION

[0003] Many varied types of non-aqueous rechargeable lithium batteries are used commercially for consumer electronics applications. Typically, these batteries employ a lithium insertion compound as the active cathode material, a lithium compound of some sort (eg. pure lithium metal, lithium alloy, or the like) as the active anode material, and a non-aqueous electrolyte. An insertion compound is a material that can act as a host solid for the reversible insertion of guest atoms (in this case, lithium atoms).

[0004] Lithium ion batteries use two different insertion compounds for the active cathode and anode materials. Presently available lithium ion batteries are high voltage systems based on $LiCoO_2$ cathode and coke or graphite anode electrochemistries. However, many other lithium transition metal oxide compounds are suitable for use as the cathode material, including $LiNiO_2$ and $LiMn_2O_4$. Also, a wide range of carbonaceous compounds is suitable for use as the anode material. These batteries employ non-aqueous electrolytes comprising $LiBF_4$ or $LiPF_6$ salts and solvent mixtures of ethylene carbonate, propylene carbonate, diethyl carbonate, and the like. Again, numerous options for the choice of salts and/or solvents in such batteries are known to exist in the art.

[0005] The excellent reversibility of this insertion makes it possible for lithium ion batteries to achieve hundreds of battery cycles. However, a gradual loss of lithium and/or buildup of impedance can still occur upon such extended cycling for various reasons. This in turn typically results in a gradual loss in delivered capacity with

cycle number. Researchers in the art have devoted substantial effort to reducing this loss in capacity. For instance, co-pending Canadian patent application serial number 2,150,877, filed June 2, 1995, and titled 'Use of P_2O_5 in Non-aqueous Rechargeable Lithium Batteries' discloses a mean for reducing this loss which involves exposing the electrolyte to P_2O_5. However, P_2O_5 shows at best only limited solubility in typical non-aqueous electrolytes and can be somewhat awkward to use in practice. Alternatives which are soluble may be more convenient, but it is unclear why such exposure is effective and hence what compounds might serve as effective alternatives.

[0006] B_2O_3 is a common chemical that is extensively used in the glass industry, and its properties are well known. B_2O_3 has also been used in the lithium battery industry for a variety of reasons. In most cases, the B_2O_3 is used as a precursor or reactant to prepare some other battery component. However, Japanese published patent application 07-142055 discloses that lithium batteries can show improved stability characteristics to high temperature storage when using lithium transition metal oxide cathodes, which contain B_2O_3. Also, co-pending Canadian patent application serial number 2,175,755, filed May 3, 1996, and titled 'Use of B_2O_3 additive in Non-aqueous Rechargeable Lithium Batteries' discloses that B_2O_3 additives can be used to reduce the rate of capacity loss with cycling in rechargeable lithium batteries and that this advantage can be obtained by having the additive dissolved in the electrolyte. However, the reason that the additive resulted in an improvement with cycling was not understood.

[0007] Co-pending Canadian patent application serial number 2,196,493, filed January 31, 1997, and titled 'Additives for Improving Cycle Life of Non-Aqueous Rechargeable Lithium Batteries' discloses a mean for reducing the rate of capacity loss with cycling, which involves exposing the electrolyte to trimethylboroxine (TMOBX). However, although TMOBX reduces the capacity fade rate, batteries comprising this compound have reduced thermal stability threshold.

[0008] Others have attempted to solve the problem of the loss of capacity with cycling by coating the surface of the cathode material with a boron compound. For instance, Sanyo's Japanese published patent application 09330720 disclosed lithium metal oxide cathodes for non-aqueous electrolyte batteries, which were coated with lithium and boron-containing compounds such as Li_3BN_2, LiB_3O_5, $LiBO_2$, $Li_2B_4O_7$. The coating was accomplished by mixing the cathode material with the boron-

containing compounds in the ratio of 10:1 moles respectively. The mixture is then heated at the high temperature of 650°C. Improved cycle performance was claimed for batteries containing such cathode materials. Ultralife's United States patent serial No.5,928,812 also disclosed the use of many lithium-containing inorganic salts such as Li_2CO_3, LiF, Li_3PO_4, $Li_2B_4O_7$, $LiBO_2$ in lithium manganese oxide cathode. However, large amounts of these salts comparable to the amount of the electrolyte salt were dispersed in the anode, separator and cathode to improve the shelf-life and the cycle life of the battery. These boron-containing salts were mixed with the cathode material without any heat treatment. In contrast, the current invention improves the capacity fade rate of a non-aqueous rechargeable lithium battery by low temperature heat-treating the lithium transition metal oxide cathode surface with small amounts of lithium boron oxide.

SUMMARY OF THE INVENTION

[0009] Rechargeable batteries exhibit a loss in delivered capacity as a function of the number of charge/discharge cycles. Herein, the fractional loss of capacity per cycle is referred to as the capacity fade rate. The instant invention includes non-aqueous rechargeable lithium batteries having reduced fade rates and methods for achieving the reduced fade rate. Non-aqueous rechargeable lithium batteries generally comprise a lithium insertion compound cathode, a lithium compound anode, and a non-aqueous electrolyte comprising a lithium salt dissolved in a non-aqueous solvent. Heat treating the surface of the cathode powder with a small amount of lithium borate at low temperature can result in improved fade rate characteristics of non-aqueous rechargeable lithium batteries.

[0010] Improved fade rates can be achieved for batteries employing otherwise conventional lithium ion battery electrochemistries. Thus, the cathode can be a lithium transition metal oxide with $LiCoO_2$ type structure, in particular the layered compound $LiCoO_2$ or $LiNi_xCo_{1-x}O_2$ ($0 \leq x \leq 1$) solid solutions. The anode can be a carbonaceous insertion compound anode, in particular graphite. The electrolyte can contain $LiPF_6$ salt dissolved in a cyclic and/or linear organic carbonate solvent, in particular mixtures containing ethylene carbonate, propylene carbonate, ethyl methyl carbonate, and/or diethyl carbonate solvents.

[0011] The cathode powder is prepared by mixing an aqueous lithium borate solution with a transition metal oxide cathode. The aqueous mixture is dried

mildly, then heated at a relative low temperature of greater than or equal to 250°C, but less than 650°C. Alternatively, a small amount of lithium borate and a transition metal oxide cathode are dry mixed thoroughly in a jar mill with media, then heated at a relative low temperature of greater than or equal to 250°C, but less than 650°C. A low heating temperature is preferable. A sufficiently small amount of lithium borate is mixed with the cathode powder such that other desirable bulk properties such as the specific capacity of the material are not adversely affected. Treating the cathode powder with lithium borate in the range of greater than 0.01%, but less than 2% of the weight of the cathode powder is effective in reducing the capacity fade rate of the battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 depicts a cross-sectional view of a preferred embodiment of a cylindrical spiral-wound lithium ion battery.\

[0013] Figure 2 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for an 18650 size battery comprising $LiBO_2$ treated $LiCoO_2$ (aqueous treatment) compared to a control cell comprising untreated $LiCoO_2$.

[0014] Figure 3 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for an 18650 size battery comprising $LiBO_2.2H_2O$ treated $LiCoO_2$ (dry-mix treatment) compared to a control cell comprising untreated $LiCoO_2$.

[0015] Figure 4 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for the series of $LiCoO_2$ cathode based 18650 size batteries comprising 0.01%, 0.1%, and 0.15% $LiBO_2$ in the cathode (aqueous treatment).

[0016] Figure 5 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for a series of $LiCoO_2$ cathode based 18650 size batteries, where the mixture of $LiCoO_2$ and $LiBO_2$ was heated at either 250°C or 450°C or 650°C (aqueous treatment).

[0017] Figure 6 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for a series of $LiCoO_2$ cathode based 18650 size batteries, where the mixture of $LiCoO_2$ and 0.15% $LiBO_2$ was heated at 600°C (dry-mix treatment) compared to a control cell comprising untreated $LiCoO_2$.

[0018] Figure 7 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for the series of $LiCoO_2$ cathode based 18650 size batteries, comprising $LiCoO_2$ blended with $LiBO_2$ powder, but not heat treated.

[0019] Figure 8 shows the Discharge Energy in Watt-hour (Wh) versus Cycle Number data for the series of $LiCoO_2$ cathode based 18650 size batteries, where $LiCoO_2$ was synthesized with and without $LiBO_2$.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS OF THE INVENTION

[0020] Throughout the following description, specific details are set forth in order to provide a more thorough understanding of the invention. However, the invention may be practiced without these particulars. In other instances, well known elements have not been shown or described in detail to avoid unnecessarily obscuring the invention. Accordingly, the specification and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

[0021] We have discovered that capacity fade rate characteristic of non-aqueous lithium rechargeable batteries can be improved by using cathode materials made from surface treated transition metal oxide cathode powder with $LiCoO_2$ type structure. The treatment consists of mixing a small amount of lithium borate with the cathode powder, then heating the mixture.

[0022] One of the methods consist of mixing an aqueous lithium borate solution with $LiCoO_2$, then the mixture is dried initially at 95°C for 1.5 hours and finally at greater than or equal to 250°C, but less than 650°C for 1.5 hours under air. Another method consists of dry-mixing a small amount of lithium borate and the transition metal oxide cathode powder in a jar mill with media for 1 hour, then heating at greater than or equal to 250°C, but less than 650°C. All heatings are performed in a box furnace (Thermcraft Incorporated). Preferably a low heating temperature is employed, so that no detrimental effect occurs to the original cathode powder. A sufficiently small amount of lithium borate is mixed with the cathode powder such that other desirable bulk properties of the battery are not adversely affected. Treating the cathode powder with lithium borate in the range of greater

than 0.01%, but less than 2% of the weight of the cathode powder is effective in reducing the capacity fade rate of the battery.

[0023] The cathode can be a lithium transition metal oxide with $LiCoO_2$ type structure, in particular the layered compound $LiCoO_2$ or $LiNi_xCo_{1-x}O_2$ ($0 \leq x \leq 1$) solid solutions. The anode can be a lithium compound. Possible anode lithium compounds include lithium metal, lithium alloys, and lithium insertion compounds. Preferred embodiments are lithium ion batteries wherein the anode is also a lithium insertion compound. Preferred electrolytes for lithium ion batteries comprise $LiPF_6$ salt dissolved in a mixture of non-aqueous cyclic and/or linear organic carbonate solvents (such as ethylene carbonate, propylene carbonate, ethyl methyl carbonate, diethyl carbonate, and/or dimethyl carbonate). The invention relates to battery constructions with cathodes comprising a cathode powder, such as $LiCoO_2$, which has been surface treated with a small amount of lithium borate. Various battery configurations are suitable, including prismatic formats or miniature coin cells. A preferred conventional construction for a lithium ion type product is depicted in the cross-sectional view of a spiral-wound battery in Figure 1. A jelly roll 4 is created by spirally winding a cathode foil 1, an anode foil 2, and two microporous polyolefin sheets 3 that act as separators.

[0024] Cathode foils are prepared by applying a mixture of a suitable powdered (about 10 micron size typically) cathode material, such as a lithiated transition metal oxide, a binder, and a conductive dilutant onto a thin aluminum foil. Typically, the application method first involves dissolving the binder in a suitable liquid carrier. Then, a slurry is prepared using this solution plus the other powdered solid components. The slurry is then coated uniformly onto the substrate foil. Afterwards, the carrier solvent is evaporated away. Often, both sides of the aluminum foil substrate are coated in this manner and subsequently the cathode foil is calendered.

[0025] Anode foils are prepared in a like manner except that a powdered (also typically about 10 micron size) carbonaceous insertion compound is used instead of the cathode material and thin copper foil is usually used instead of aluminum. Anodes are typically slightly wider than the cathode in order to ensure that there is always anode opposite cathode.

[0026] The jelly roll 4 is inserted into a conventional battery can 10. A header 11 and gasket 12 are used to seal the battery 15. The header may include safety devices if desired such as a combination safety vent and pressure operated disconnect device. Additionally, a positive thermal coefficient device (PTC) may be incorporated into the header to limit the short circuit current capability of the battery. The external surface of the header 11 is used as the positive terminal, while the external surface of the can 10 serves as the negative terminal.

[0027] Appropriate cathode tab 6 and anode tab 7 connections are made to connect the internal electrodes to the external terminals. Appropriate insulating pieces 8 and 9 may be inserted to prevent the possibility of internal shorting.

[0028] Prior to crimping the header 11 to the can 10 and sealing the battery, the electrolyte 5 is added to fill the porous spaces in the jelly roll 4.

[0029] At this point, the battery is in a fully discharged state. Generally, an electrical conditioning step, involving at least a single complete recharge of the battery, is performed immediately after assembly. One of the reasons for so doing is that some initial irreversible processes take place during this first recharge. For instance, a small amount of lithium is irreversibly lost during the first lithiation of the carbonaceous anode.

[0030] The advantages of the invention can be achieved using small amounts of lithium borate to treat the surface of the cathode powder. In the examples to follow, desirable results were obtained using on the order of 0.01% to 0.15% lithium borate by weight of the cathode powder. Reduced cell capacity can be expected if excessive amounts of lithium borate are employed. Therefore, some straightforward quantification trials were required in order to select an appropriate amount lithium borate to use.

[0031] At this time, the reason for the fade rate improvement using lithium borate is unclear. Without being adversely bound by theory, but wishing to enable the reader to better understand the invention, a possible explanation is that during the low temperature heating, lithium borate is dispersed on the surface of $LiCoO_2$ where it has a stabilizing effect, thereby reducing the capacity fade rate.

[0032] The term 'lithium borate' is used herein to refer to any lithium-boron-oxide compound including $LiBO_2$, LiB_3O_5, $Li_2B_4O_7$ and hydrates thereof. Mixtures of lithium and boron compounds that react or decompose to form lithium borate compounds at temperatures of greater or equal to 250°C, but less than 650°C can also be expected to provide similar benefits.

[0033] The following Examples are provided to illustrate certain aspects of the invention but should not be construed as limiting in any way. 18650 size cylindrical batteries (18 mm diameter, 65 mm height) were fabricated as described in the preceding and shown generally in Figure 1. Cathodes 1 comprised a mixture of lithium borate-surface-treated-transition metal oxide powder, a carbonaceous conductive dilutant, and polyvinylidene fluoride (PVDF) binder that was uniformly coated on both sides of a thin aluminum foil. The transition metal oxides used was $LiCoO_2$ as indicated below. Anodes 2 were made using a mixture of a spherical graphitic powder plus Super S (trademark of Ensagri) carbon black and PVDF binder that was uniformly coated on thin copper foil. Celgard 2300® microporous polyolefin film was used as the separator 3.

[0034] The electrolytes 5 employed were solutions of 1M $LiPF_6$ salt dissolved in a solvent mixture of ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) solvents in a volume ratio of 30/20/50 respectively.

[0035] To protect against hazardous conditions on overcharge of the battery, the header of these batteries included a pressure operated electrical disconnect device. The electrolytes employed also contained 2.5 % biphenyl additive by weight to act as a gassing agent for purposes of activating the electrical disconnect device (in accordance with the disclosure in co-pending Canadian Patent Application Serial No. 2,163,187, filed November 17, 1995, titled 'Aromatic Monomer Gassing Agents for Protecting Non-aqueous Lithium Batteries Against Overcharge', by the same applicant).

[0036] For the examples that follow, note that the control batteries employ $LiCoO_2$ as received from the manufacturers. For each of the examples below one distinct batch of $LiCoO_2$ powder was used to prepare all the treated $LiCoO_2$ powders described within that example. Different examples may use different batches of $LiCoO_2$.

Example I - cathodes with $LiBO_2$ treated $LiCoO_2$

[0037] $LiCoO_2$ cathode based 18650 batteries were assembled using $LiCoO_2$ treated with aqueous 0.05% $LiBO_2$. The treatment consisted of first dispersing 0.4g of $LiBO_2$ powder in about 210mL of water and stirring for about 10 minutes. The solution turns cloudy as $LiBO_2$ is not so soluble. About 800g of $LiCoO_2$ was then added to this solution and stirred for an additional 10 minutes. The mixture was then dried initially at 95°C for about 1.5 hours and finally at 250°C for 1.5 hours under air. Heating was performed in a box furnace from Thermcraft Incorporated.

[0038] For electrical testing, the batteries were thermostatted at 21 ±1°C. Cycling was performed using 1.5A constant voltage recharge for 2.5 hours to 4.2V and 1.65A constant current discharge to 2.5V cutoff. Note that for purposes of observing changes in battery impedance, a prolonged, low rate charging or discharging was performed every 10 cycles (alternating between charging and discharging). Subsequent discharge capacities may then be significantly different from the previous ones. These points have been omitted from the data presented below for purposes of clarity. However, this type of testing can introduce a noticeable discontinuity in the capacity versus cycle number data curves.

[0039] The batteries with treated $LiCoO_2$ are compared with control batteries in Figure 2, where discharge energy (Wh) versus cycle number data for each battery is plotted. The capacity fade rate of batteries with $LiBO_2$-surface treated cathode material is superior to the control batteries.

[0040] Similarly but using the dry-mix treatment, $LiCoO_2$ cathode based 18650 batteries were assembled using $LiCoO_2$ treated with 0.4% $LiBO_2.2H_2O$ by weight of the cathode powder. $LiCoO_2$ and $LiBO_2.2H_2O$ were thoroughly dry-mixed in a jar mill with media for 1 hour, then heated at 250°C in a furnace (Thermcraft Incorporated) for 1.5 hours under air. The batteries were then cycled as described above. Figure 3 shows the discharge energy (Wh) versus cycle number data for each battery. The capacity fade rates of the surface treated cathode batteries were better than the control batteries.

[0041] This example shows that the aqueous and the dry-mix treatments of $LiCoO_2$ with lithium borate improve the capacity fade rate.

Example II - cathodes treated with different amounts of LiBO2

[0042] Another series of $LiCoO_2$ cathode based 18650 batteries were assembled with cathodes comprising $LiCoO_2$ heat treated with various amounts of $LiBO_2$. The same aqueous treatment procedure was followed as for Example I, except that the amounts of $LiBO_2$ were 0.01%, 0.1% and 0.15% $LiBO_2$ by weight of $LiCoO_2$ powder. The batteries were cycled as in Example I. Figure 4 shows the discharge energy (Wh) versus cycle number data for each battery. The capacity fade rate of all the batteries containing cathode material treated with $LiBO_2$ was better than the controls. The improvement was most prominent for the 0.1% and 0.15% $LiBO_2$ batteries.

Example III - cathodes treated with $LiBO_2$ heated
at 250°C, 450°C or 650°C (aqueous treatment)

[0043] Cylindrical 18650 batteries were assembled with cathodes comprising $LiCoO_2$ heat treated with 0.15% $LiBO_2$ by weight of the cathode powder. The same aqueous treatment procedure was followed as for Example I, except one batch of cathode powder had the final heating temperature at 250°C, another at 450°C and yet another at 650°C. The batteries were cycled as described in Example I. Figure 5 shows the discharge energy (Wh) versus cycle number data for each battery. The batteries with cathode powder heated at 650°C had worse capacity fade rate than either the control or the batteries with cathode powder heated at 250°C or at 450°C. The capacity fade rates of the 250°C and 450°C treated $LiCoO_2$ batteries were similar and substantially improved over that of the controls. This example shows that excessive heating temperature during the surface treatment is undesirable.

Example IV - cathodes treated with $LiBO_2$
heated at 600°C (dry-mix treatment)

[0044] Cylindrical 18650 batteries were assembled with cathodes comprising $LiCoO_2$ heat treated with 0.15% $LiBO_2$ by weight of the cathode powder. The same dry-mix treatment procedure was followed as for Example I, except the cathode powder was heated at 600°C instead of 250°C. The batteries were cycled as described in Example I. Figure 6 shows the discharge energy (Wh) versus cycle number data for the batteries. The capacity fade rate of the $LiBO_2$ treated $LiCoO_2$ batteries were better than the controls. This example shows that the dry-mixing and heating $LiCoO_2$ and a small amount of $LiBO_2$ at 600°C also improved the capacity fade rate.

Comparative Example I - cathodes with $LiCoO_2$ and $LiBO_2$, blended but not heat treated

[0045] Cylindrical 18650 batteries were assembled with cathodes comprising $LiCoO_2$ mixed with 0.4%$LiBO_2$ by weight of the cathode powder, but not heat treated. The $LiBO_2$ was blended with $LiCoO_2$ and the mixture was used as the cathode powder. The batteries were cycled as described in Example I. Figure 7 shows the discharge energy (Wh) versus cycle number data for each battery. The capacity fade rate of batteries made with the blended powder and the control batteries were about the same. No improvement was observed. This example shows that prior art methods of preparing the cathode powder by blending $LiBO_2$ and $LiCoO_2$ do not improve the capacity fade rate.

Comparative Example II - cathodes with $LiBO_2$ included during synthesis of LiCoO2

[0046] Cylindrical 18650 batteries were assembled with cathodes comprising $LiCoO_2$ synthesized with various amounts of $LiBO_2$. $LiCoO_2$ was prepared from a stoichiometric mixture of Li_2CO_3 and Co_3O_4 with various amounts of $LiBO_2$ (0.4%, 0.8%, 1.5% by weight of the $LiCoO_2$ product) included in the reaction mix. The powders were blended, jar-milled for 1 hr, then heated in a box furnace at 850°C for 2 hours under air. The product was ground and sifted through a 100 mesh screen; further heated at 850°C for 8 hours under air, then finally ground and sifted through a 200 mesh screen. The $LiCoO_2$ synthesized with various amounts of $LiBO_2$ was used to prepare cathodes which were assembled into batteries, which were cycled as described in Example I. Figure 8 shows the discharge energy (Wh) versus cycle number data for each battery. The capacity fade rate of both the synthesized powders and the control batteries were about the same. No improvement in the capacity fade was observed by the addition of $LiBO_2$ in the synthesis of $LiCoO_2$. This example shows that prior art methods of preparing $LiCoO_2$ with $LiBO_2$ included in the reaction mix does not improve the capacity fade rate.

[0047] The preceding examples demonstrate that surface treatment of $LiCoO_2$ with a small amount of lithium borate can improve the capacity fade rate of non-aqueous rechargeable lithium batteries.

[0048] As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the

invention is to be construed in accordance with the substance defined by the following claims.